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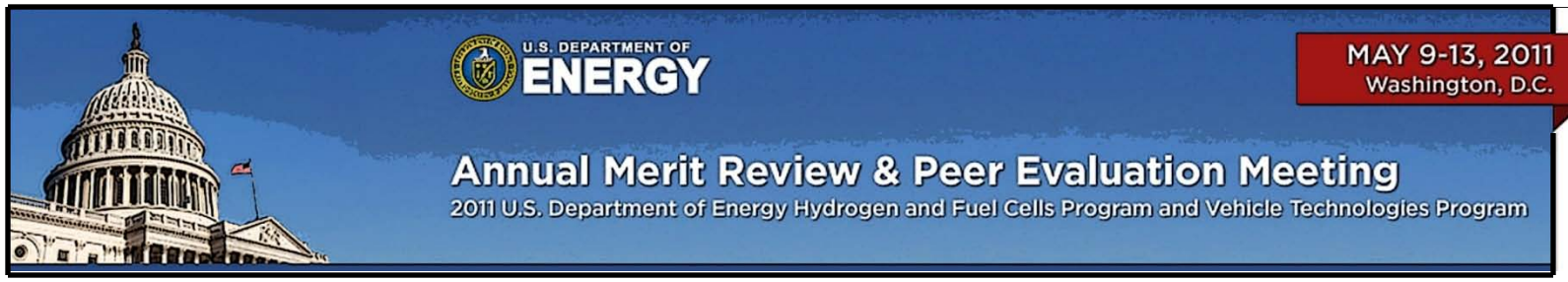

Inexpensive, Nonfluorinated (or Partially Fluorinated) Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

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Ionic Liquids & Electrolytes for Energy Storage (ILEET) Laboratory
Department of Chemical & Biomolecular Engineering
NC State University

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Project ID# es057

NC STATE UNIVERSITY

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Overview

Timeline

Project Start: April 24, 2009

Project End: March 31, 2012

Percent Completed: 66%

Barriers

Low cost cell materials

Abuse tolerance

Low temperature performance

Budget

Total Project Funding:

$763,057

Funding Received FY10:

$245,450

Funding Received FY11:

$245,882

Partners

Project Lead: Wesley Henderson

Co-PIs: Michel Armand, Peter Fedkiw

Collaborators:

- Kang Xu, Richard Jow (ARL)
- Patrick Judeinstein (Université Paris-Sud)
- Steve Greenbaum (Hunter College of CUNY)
- Patrik Johansson (Chalmers University)

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Objectives

- Develop techniques to synthesize electrolytes that allow for lower cost of production
- Develop low-cost, thermally stable electrolytes to replace ones now commonly used
- Develop electrolyte/additive combinations that will facilitate a more stable solid-electrolyte interphase (SEI) on the anode
- Develop additives that allow for the formation of protective coatings on the cathode (i.e., a cathode SEI) and enhances electrochemical stability above 4.3 V

Milestones

Milestone	Completion
Characterization (properties/phase diagrams) of solvent-$LiBF_4$ mixtures as model electrolytes	ongoing
Characterization (properties/phase diagrams) of solvent-LiBOB and -LiDFOB mixtures to examine structural effects on solubility/properties	ongoing
Synthesis/characterization of ionic liquids containing cyanocarbanions and $DFOB^-$	ongoing
Synthesis of new partially fluorinated anions (with new ligands) and cyanocarbanions	ongoing

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Approach

Synthesize and fully characterize two classes of nonfluorinated (or less fluorinated) anions:

(1) chelated and non-chelated organoborate anions (related to bis(oxalato) borate or BOB^-), and

(2) Hückle-type anions in which the charge is stabilized on a 5-member azole ring and noncyclic cyanocarbanions. Characterize the physical properties of these new anions, incorporated in both lithium salts and ionic liquids, by examining the thermal phase behavior (phase diagrams); thermal, chemical and electrochemical stability; transport properties; interfacial properties; molecular interactions and cell performance. These salts will be compared with widely used salts such as $LiPF_6$ and LiBOB and ionic liquids based upon the bis(trifluoromethanesulfonyl)imide anion ($TFSI^-$).

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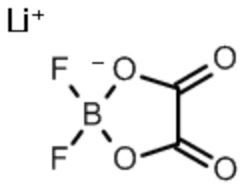
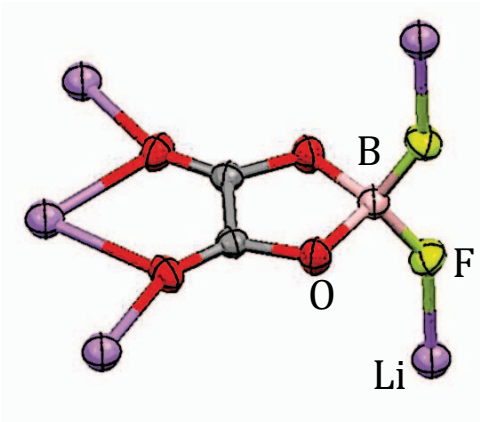
Technical Accomplishments - Overview

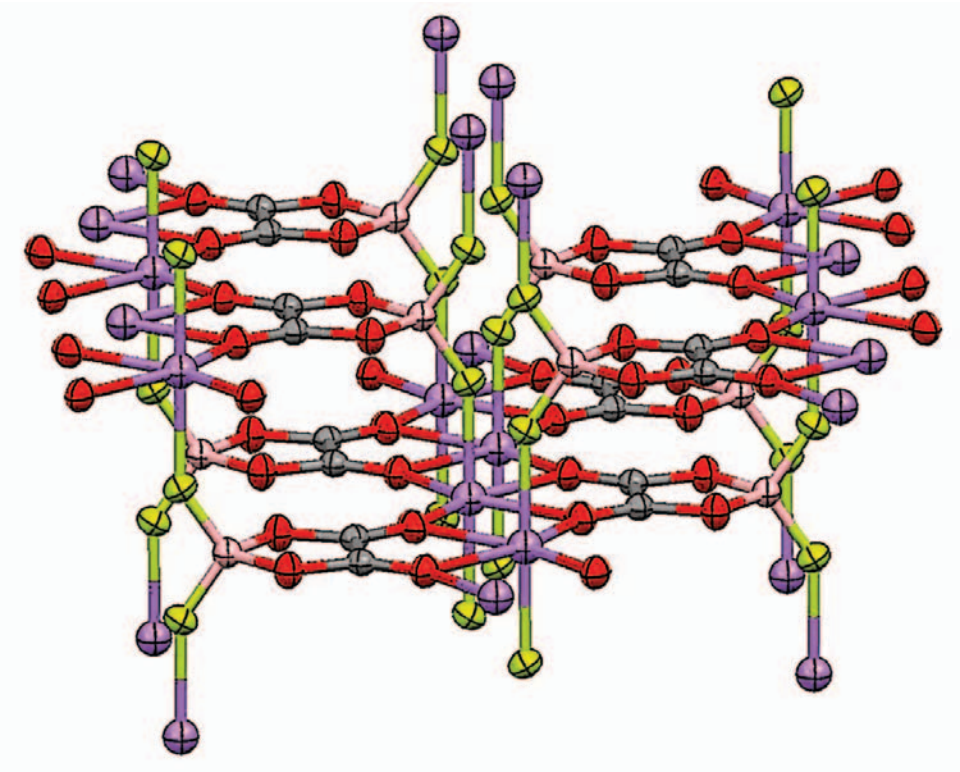
- Prepared phase diagrams of solvent-$LiBF_4$ mixtures (acetonitrile, adiponitrile) to serve as a model system (for comparison with new salts)
- Synthesized high purity lithium difluoro(oxalato)borate (LiDFOB) – determined the crystal structure of the LiDFOB·$2H_2O$ dihydrate – prepared phase diagrams with a variety of solvents including carbonates, esters, sulfones and nitriles/dinitriles – numerous LiDFOB solvate crystal structures were determined providing insight into how the anion and solvent molecules interaction with Li^+ cations
- Characterized ionic liquid (IL) properties (conductivity, density, viscosity, diffusion coefficients) for ILs with cyanocarbanions: $DCTA^-$ (dicyanotriazolate) and DCA^- (dicyanamide)

Lithium Difluoro(oxalato)borate (LiDFOB)





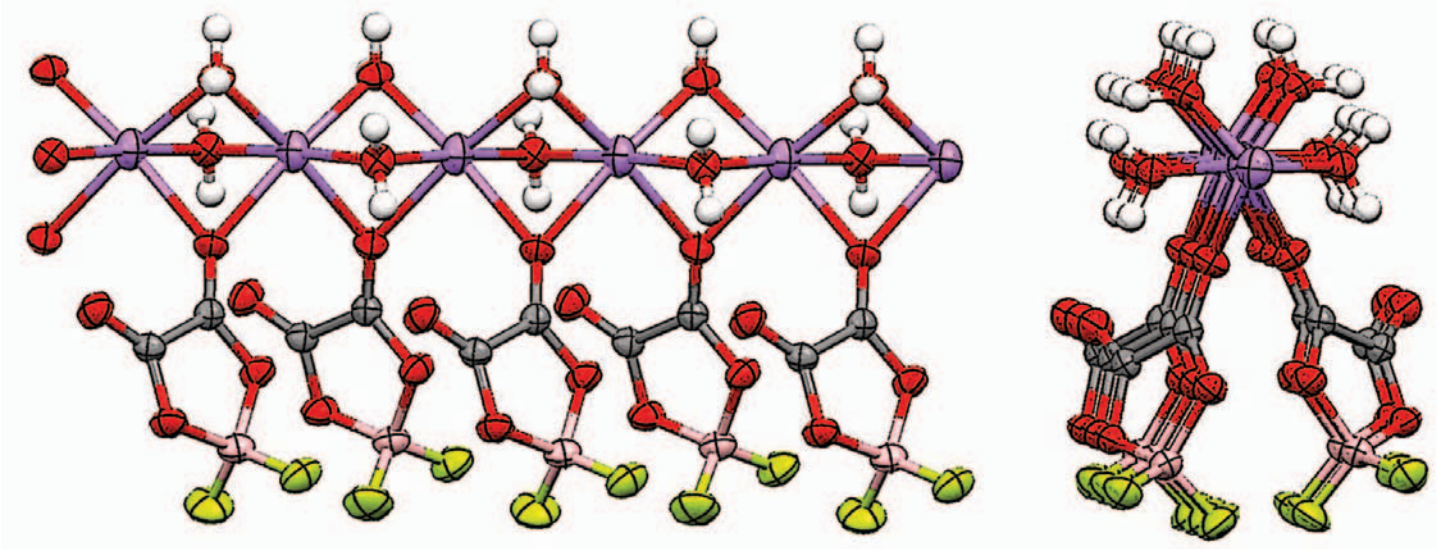
Crystal structure of LiDFOB



LiDFOB·2H_2O

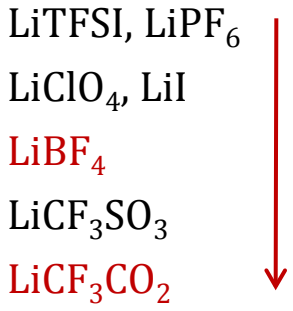
Crystal structure of
LiDFOB dihydrate

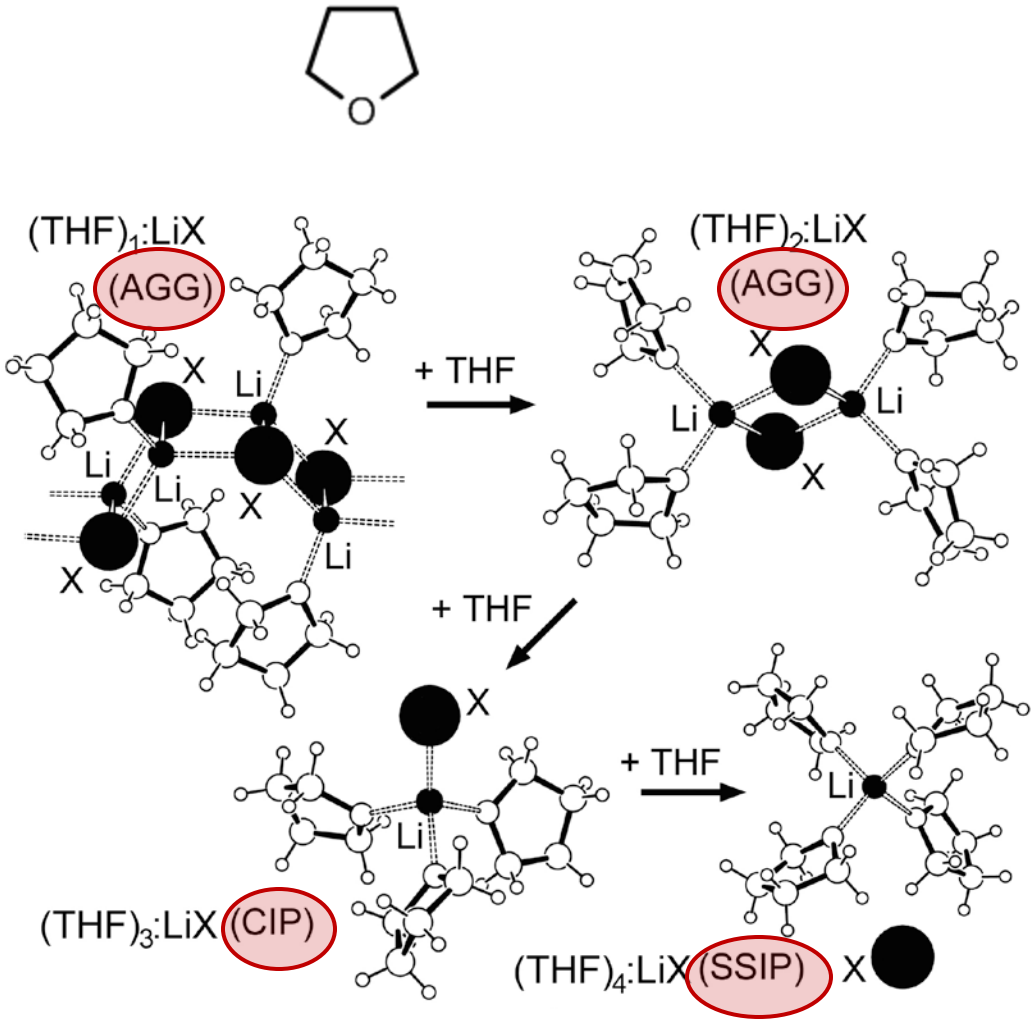
CIP $(H_2O)_2$:LiDFOB



$(Solvent)_n$-LiX Mixtures: Ionic Association Interactions

- Solvent-Separated Ion Pairs (SSIPs)
  (uncoordinated anions)
- Contact Ion Pairs (CIPs)
  (anion coordinated to 1 Li^+)
- Aggregates (AGGs)
  (anion coordinated to 2 or more Li^+)





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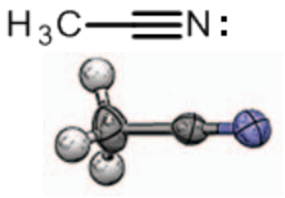
AN-Li$^+$ Solvation



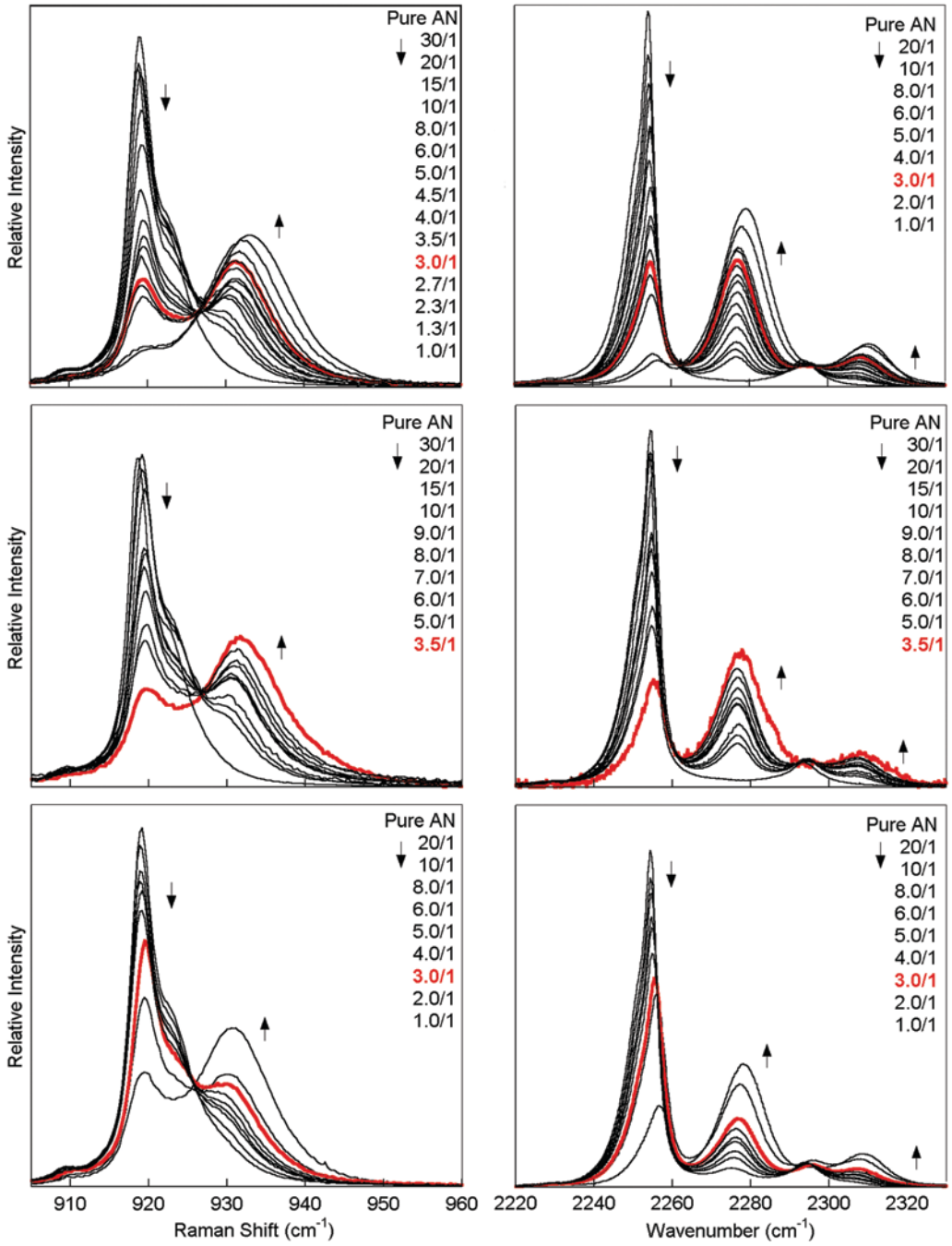
C-C stretching mode (920 cm^{-1})

C≡N stretching mode (2250 cm^{-1})

LiBF$_4$

LiDFOB

LiCF$_3$CO$_2$



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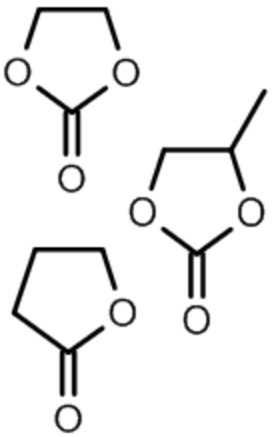
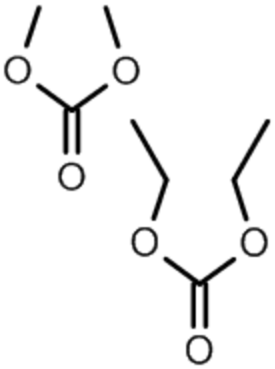
Carbonate & Ester Solvents



ethylene carbonate (T_m 35°C, T_b 244 C)

propylene carbonate (T_m -55°C, T_b 242 C)

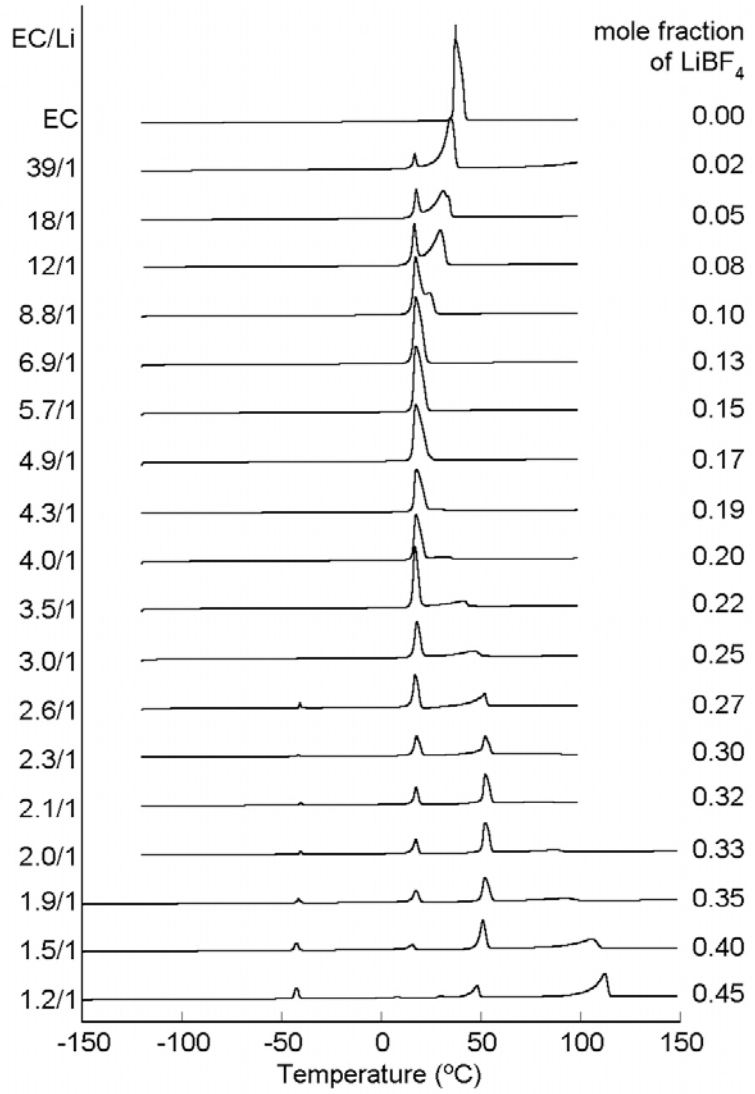
γ-butyrolactone (T_m -44°C, T_b 204 C)

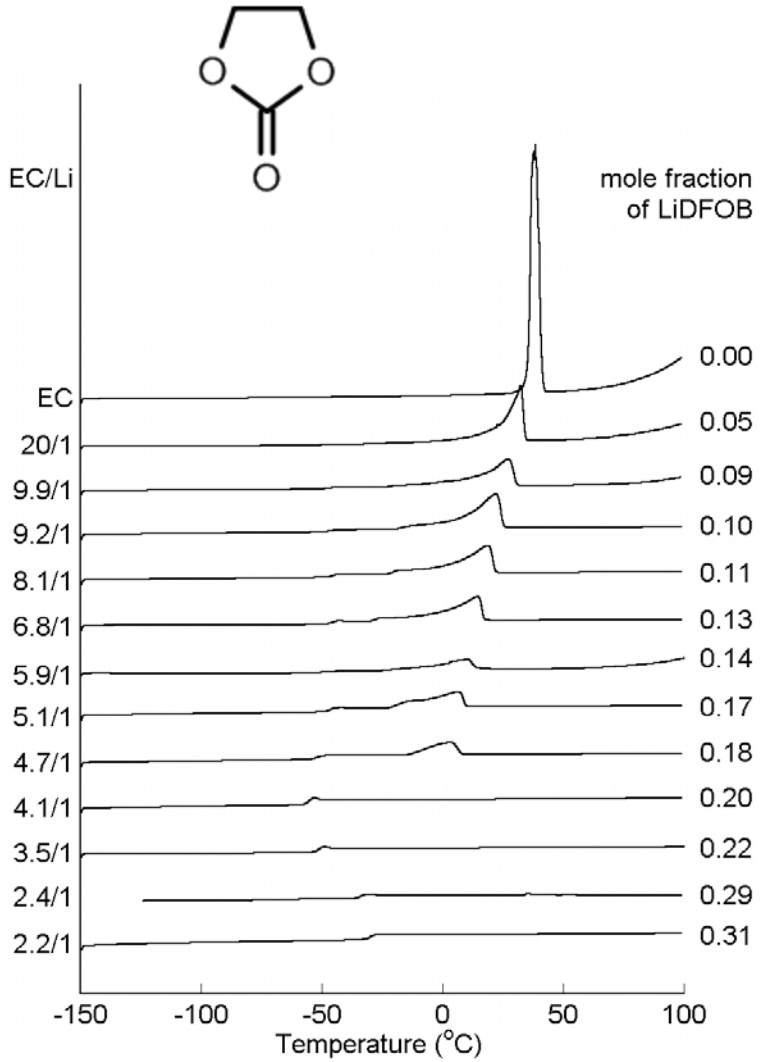


dimethyl carbonate (T_m 5°C, T_b 91 C)

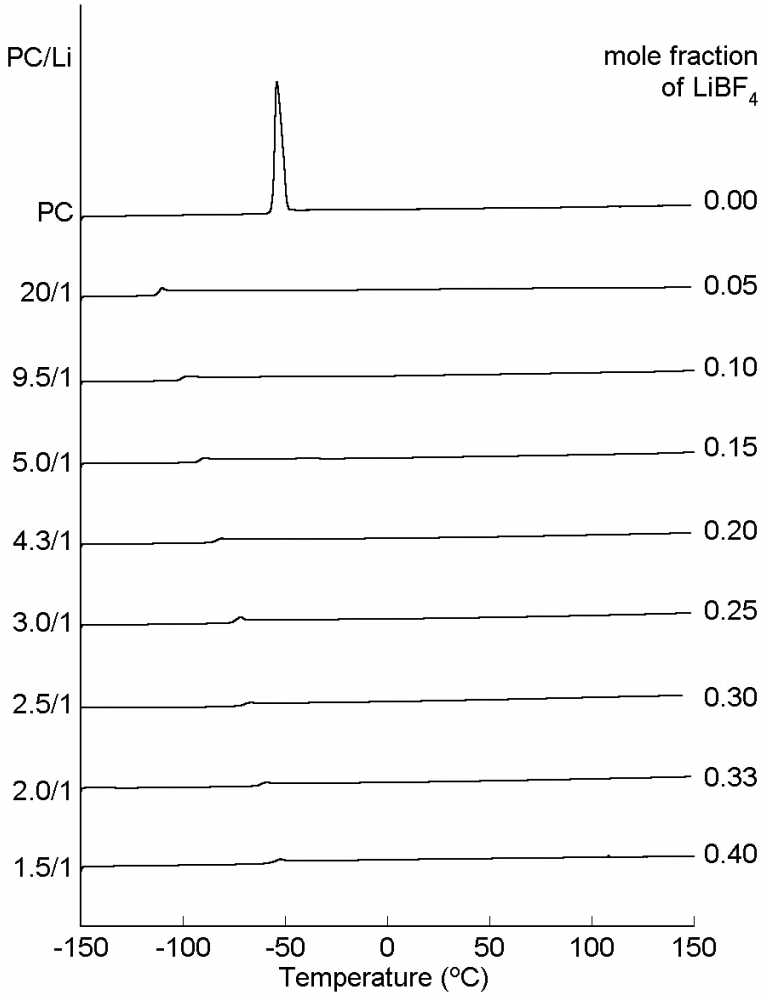
diethyl carbonate (T_m -74°C, T_b 126 C)

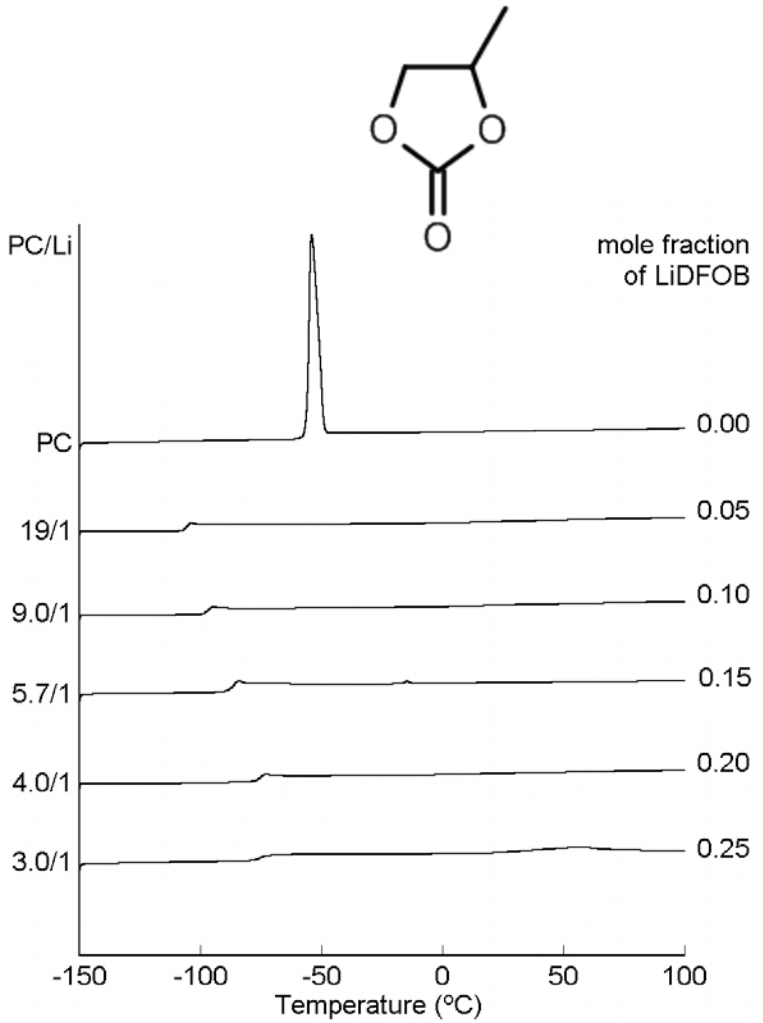
Ethylene Carbonate $(EC)_n$-LiX Phase Behavior



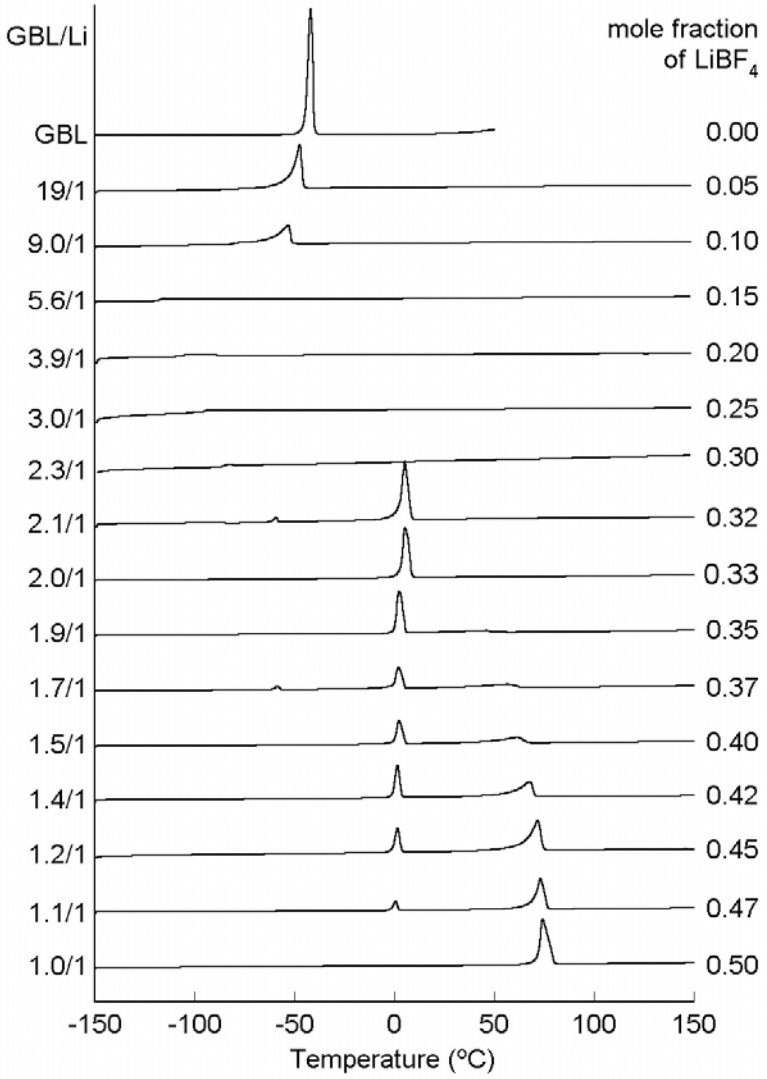


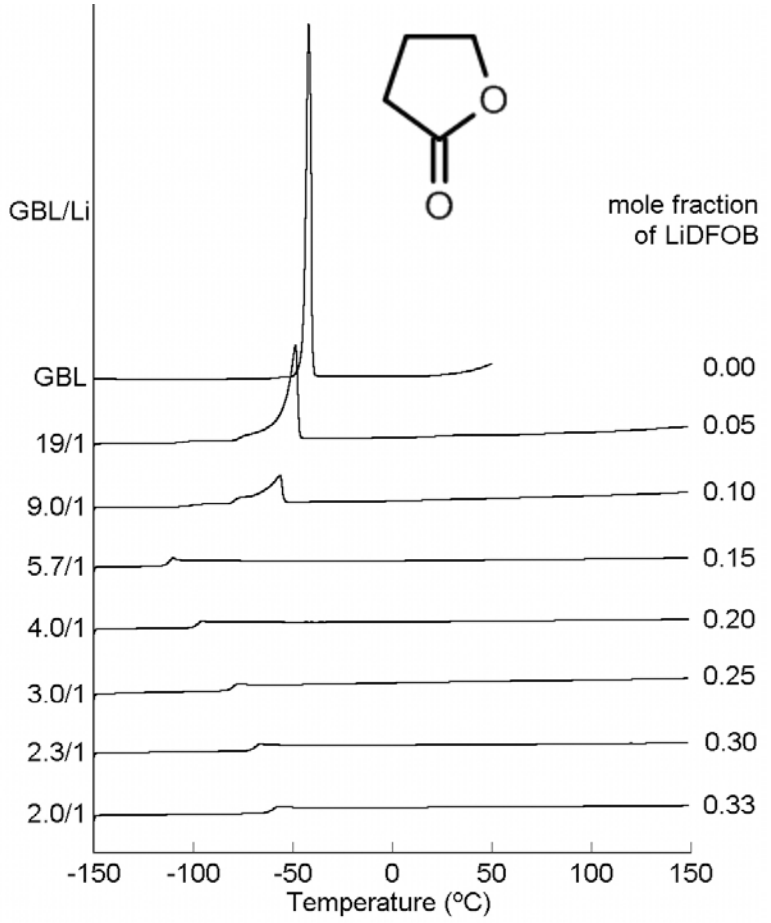
Propylene Carbonate $(PC)_n$-LiX Phase Behavior



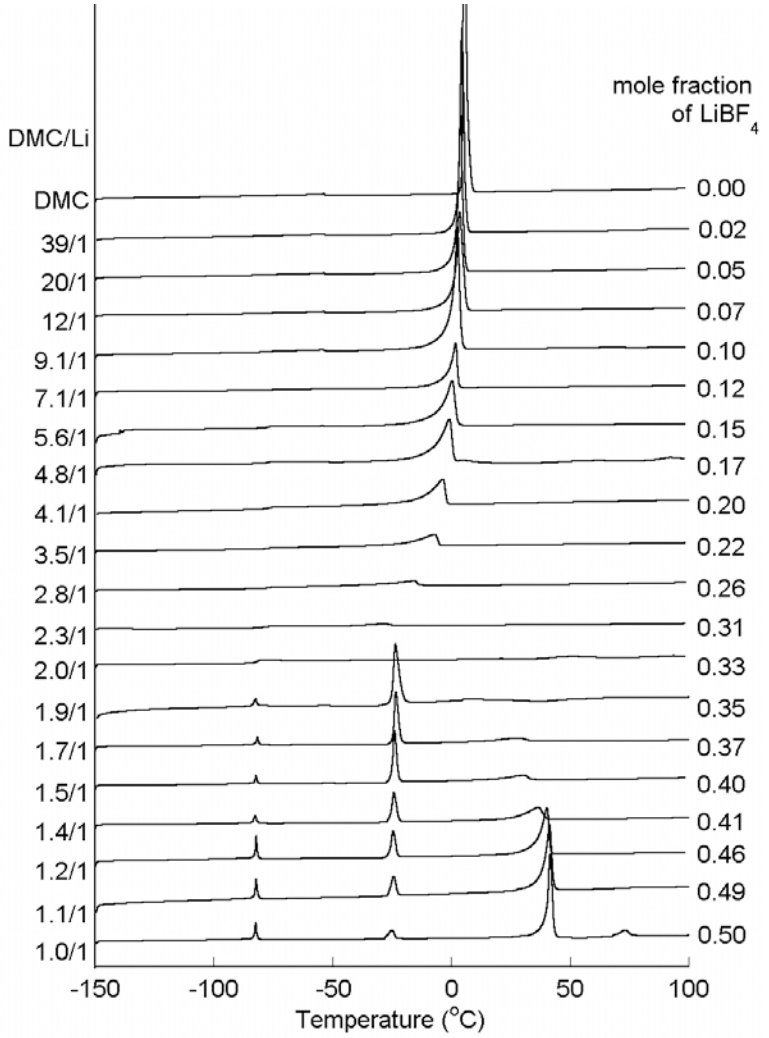


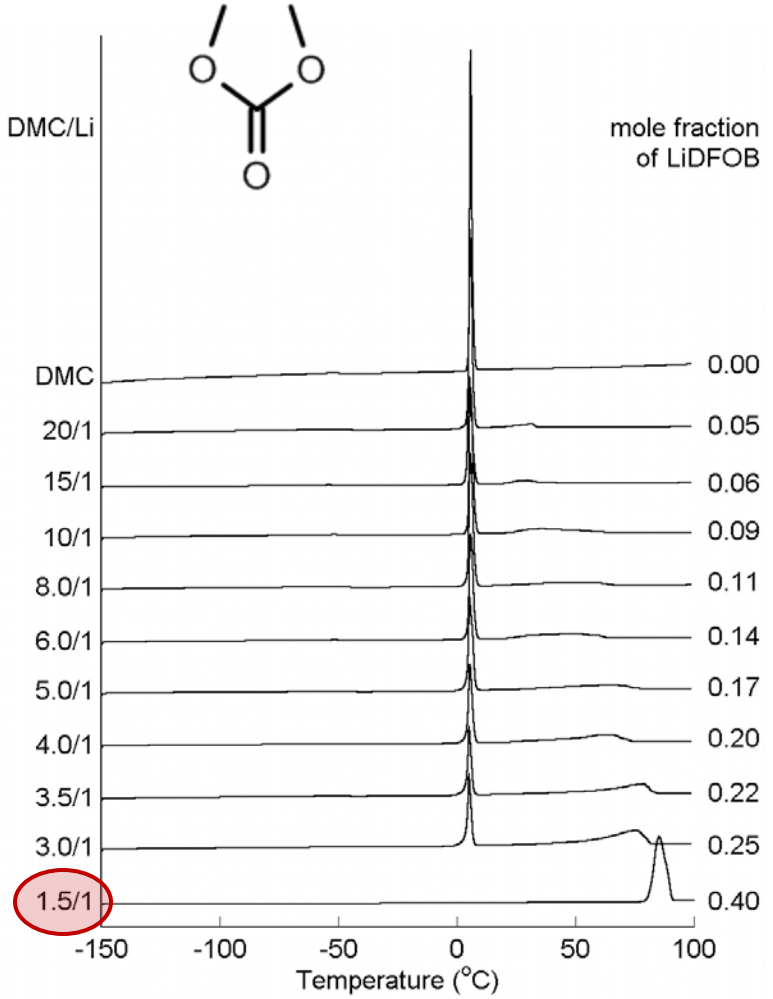
γ-Butyrolactone $(GBL)_n$-LiX Phase Behavior



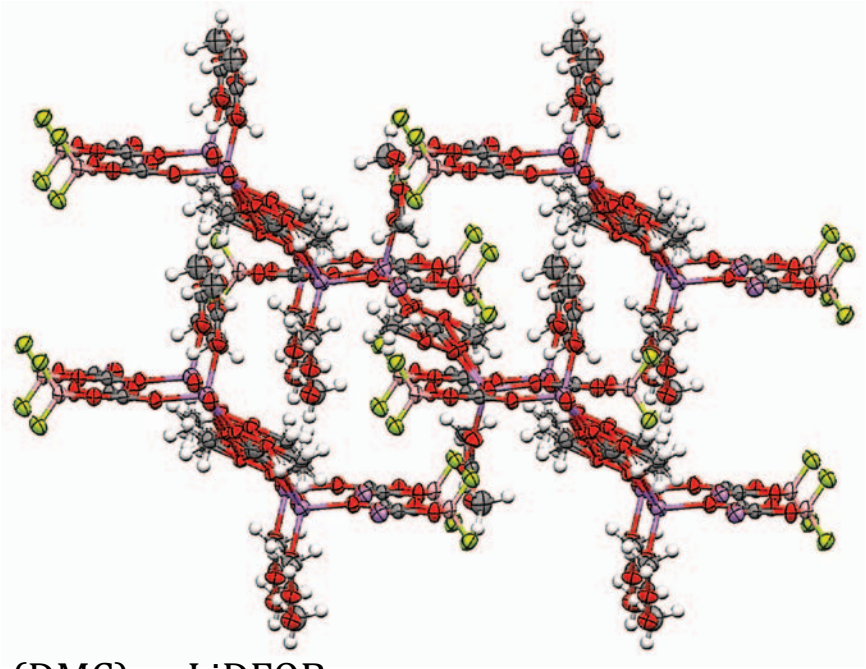


Dimethyl Carbonate $(DMC)_n$-LiX Phase Behavior

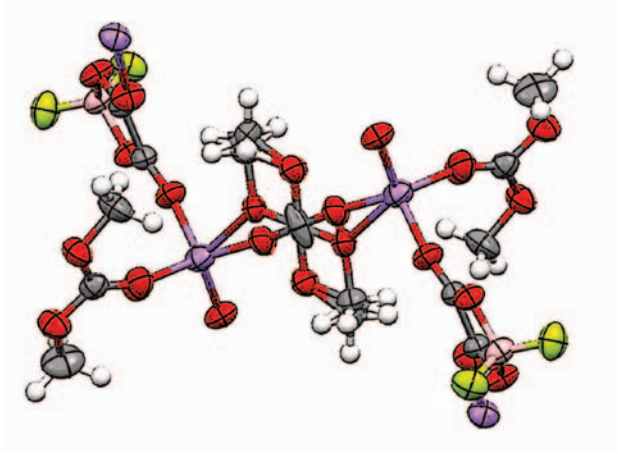


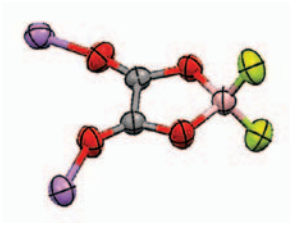


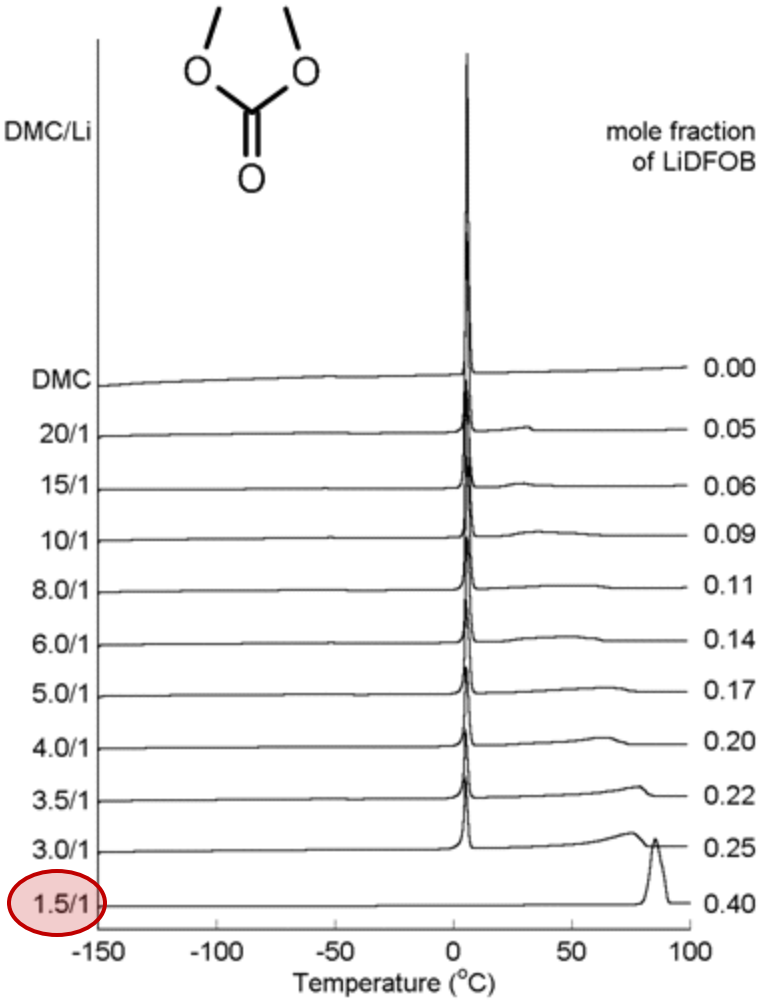
Dimethyl Carbonate $(DMC)_n$-LiX Phase Behavior



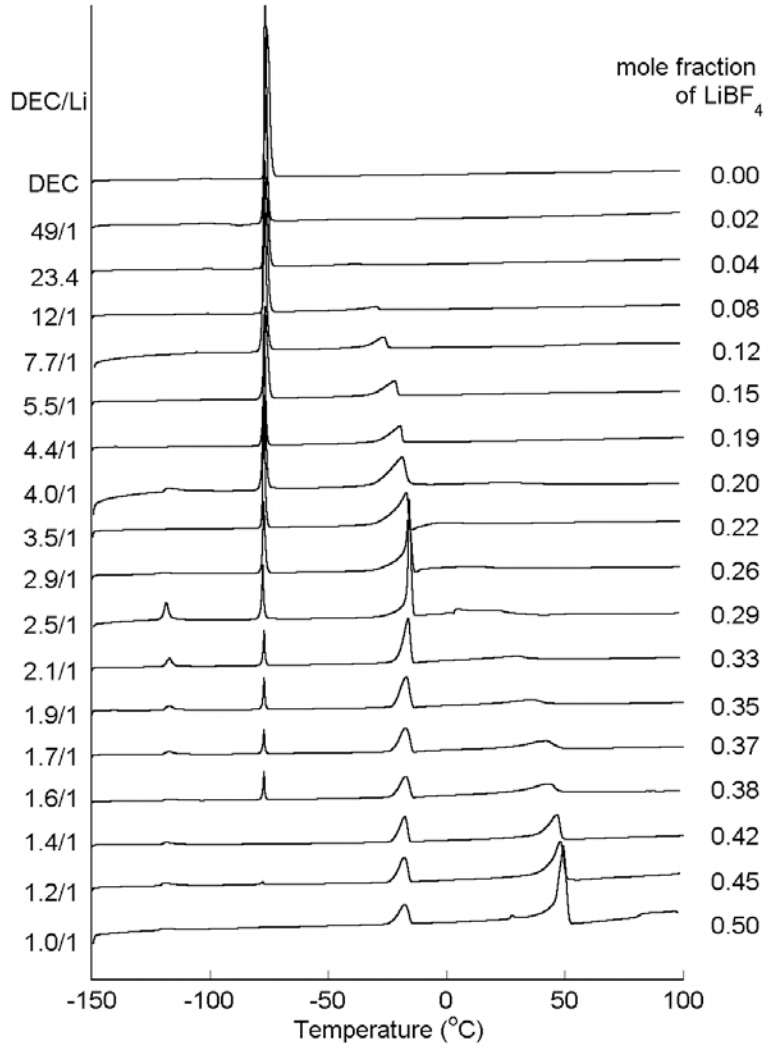
AGG $(DMC)_{3/2}$:LiDFOB

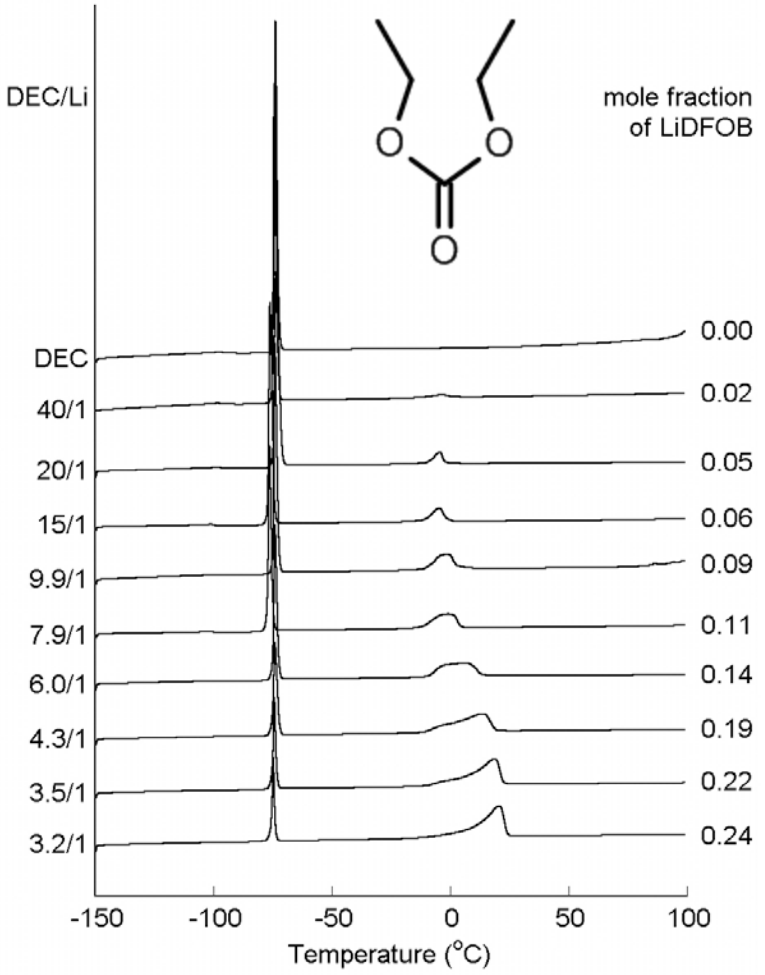




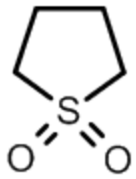


Diethyl Carbonate $(DEC)_n$-LiX Phase Behavior

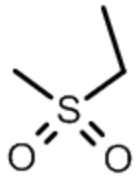




Sulfone Solvents for High-Voltage Electrolytes



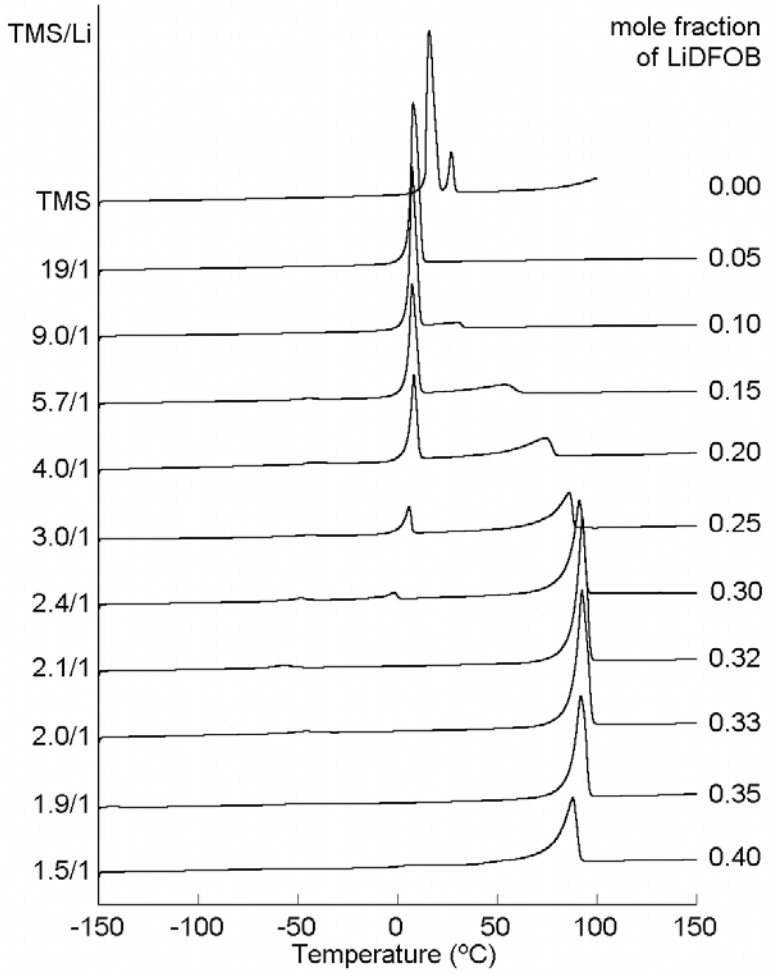
tetramethylene sulfone (T_m 27°C, T_b 285 C)

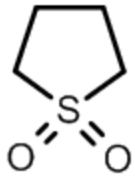


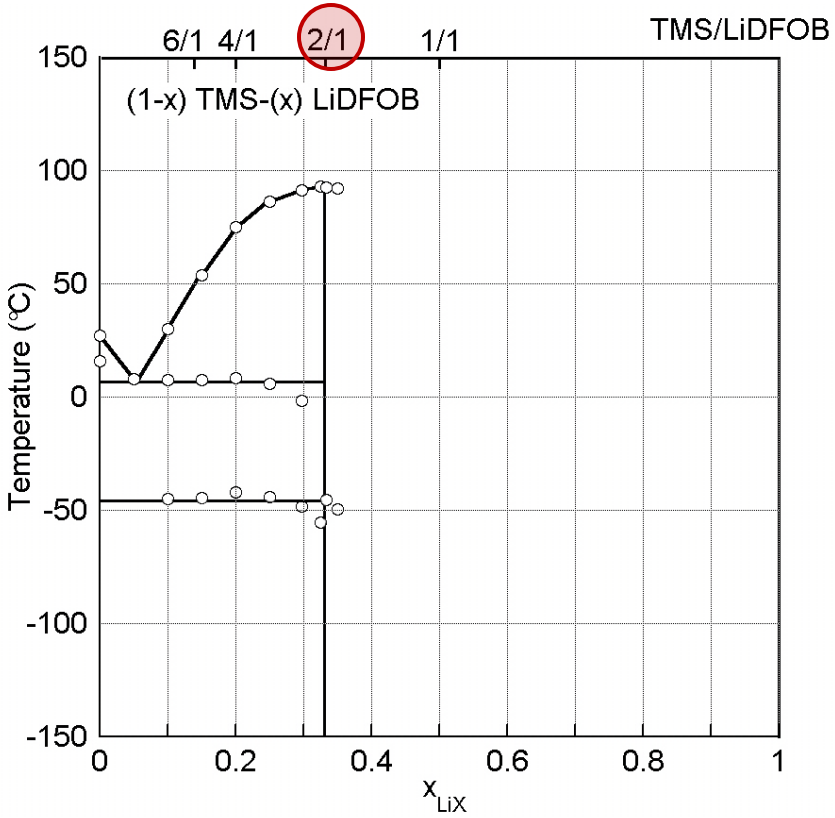
ethyl methyl sulfone (T_m 32-37°C, T_b ??? C)

- A. Abouimrane, I. Belharouak, K. Amine, *Electrochem. Commun.* **2009**, *11*, 1073

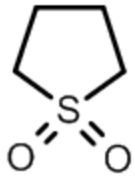
Sulfone-LiDFOB Phase Behavior



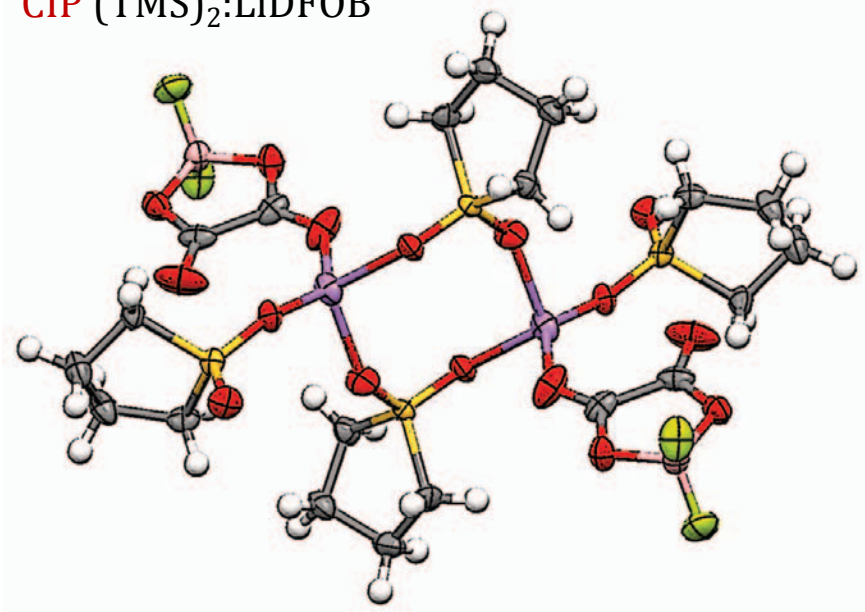


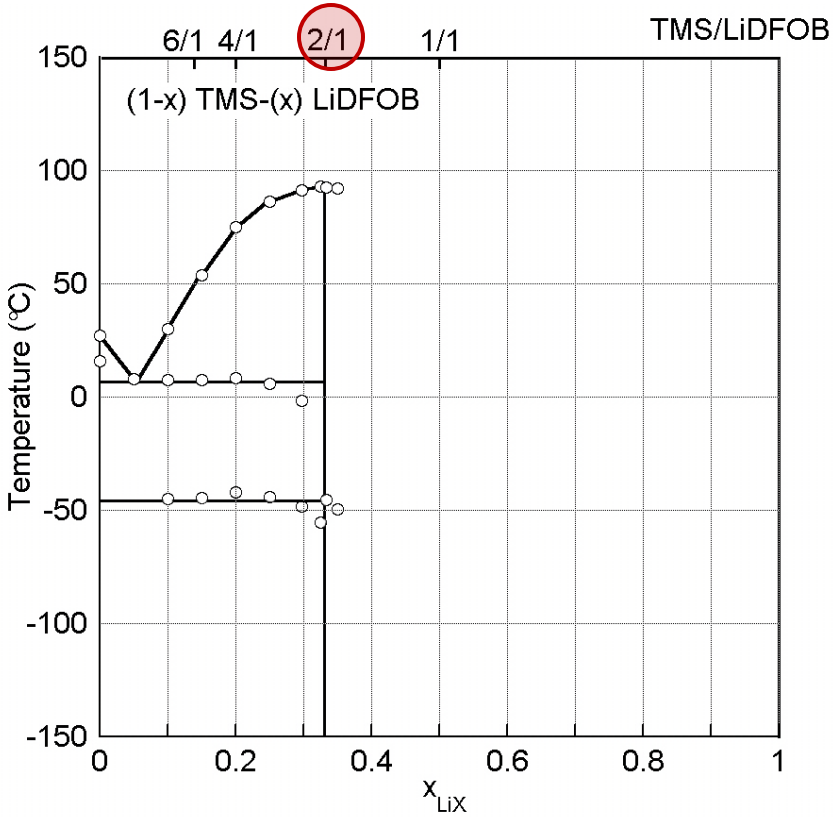


$(TMS)_n$-LiDFOB Phase Behavior

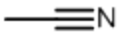


CIP $(TMS)_2$:LiDFOB



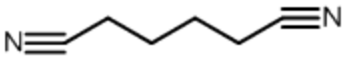


Nitrile/Dinitrile Solvents for High-Voltage Electrolytes



acetonitrile (T_m -45°C, T_b 82 C)

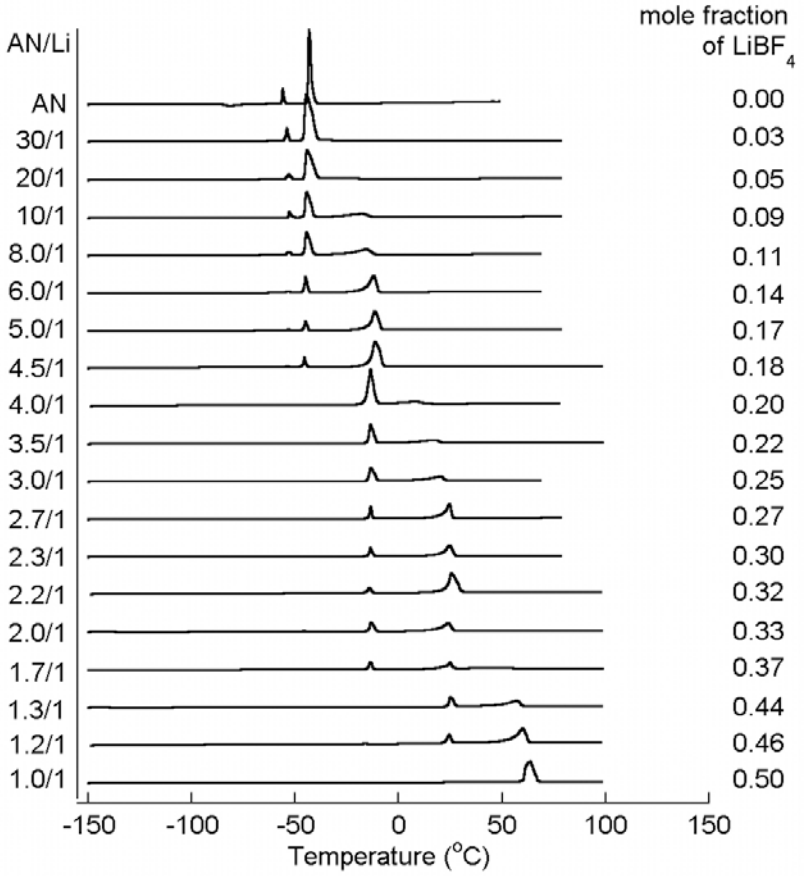
glutaronitrile (T_m -29°C, T_b 286 C)

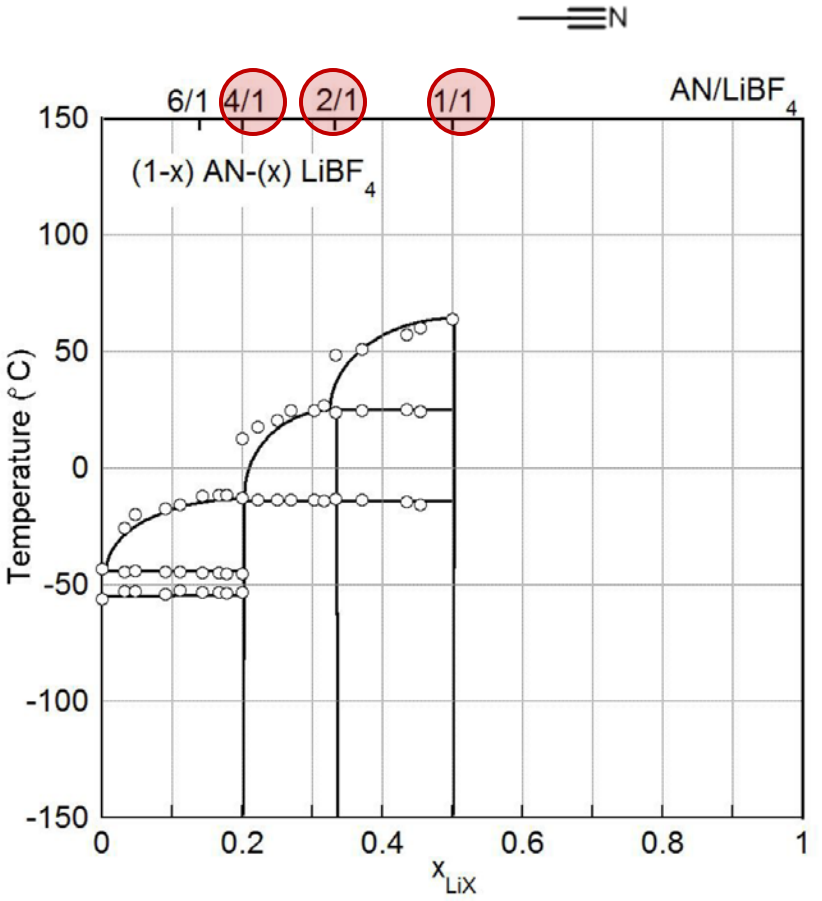


adiponitrile (T_m 4°C, T_b 295 C)

- Y. Abu-Lebdeh and I. Davidson, *J. Electrochem. Soc.* **2009**, *156*, A60

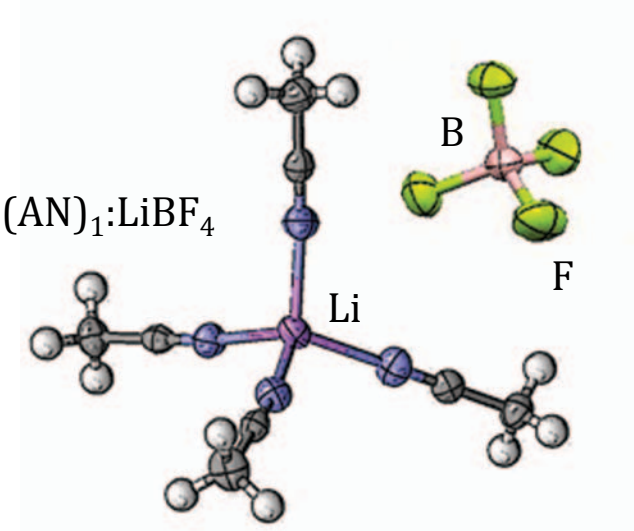
Acetonitrile (AN)-$LiBF_4$ Phase Behavior



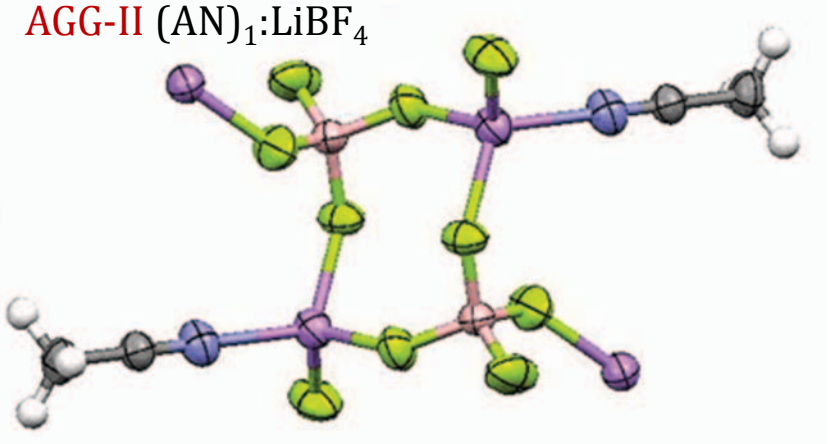


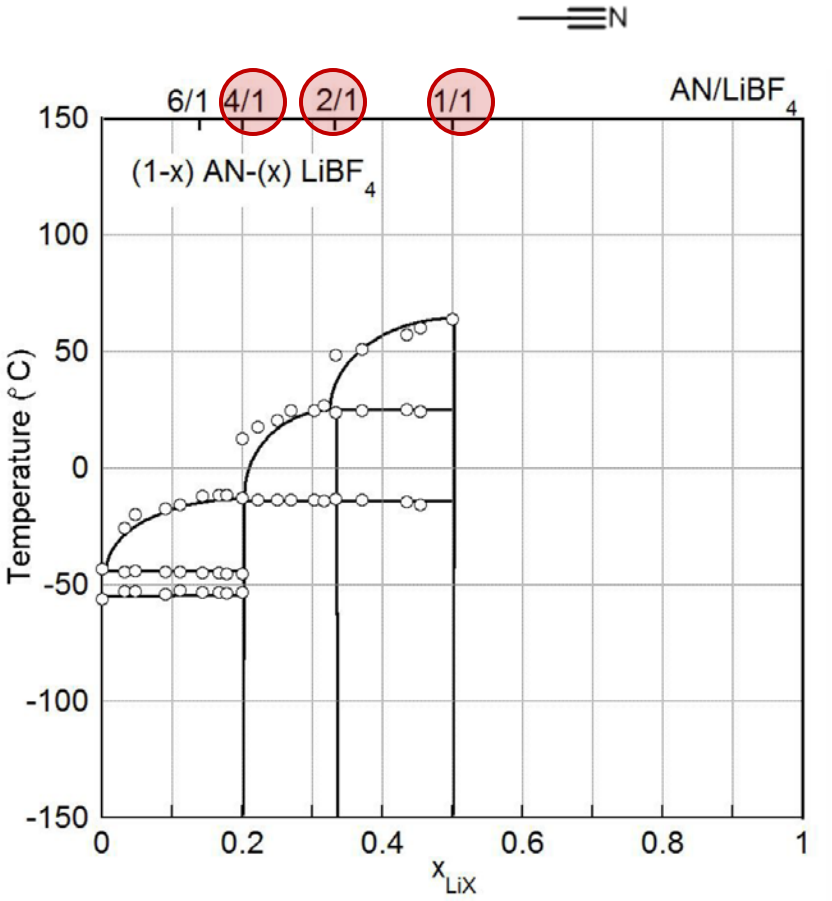
Acetonitrile $(AN)_n$-$LiBF_4$ Phase Behavior

SSIP $(AN)_1$:$LiBF_4$

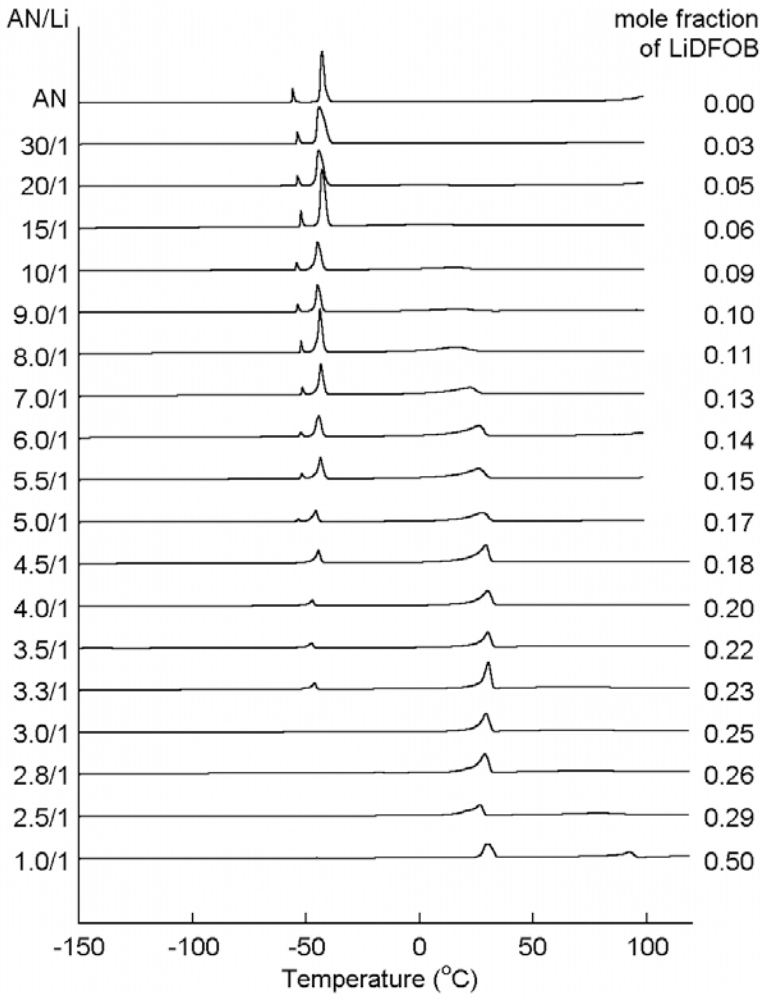


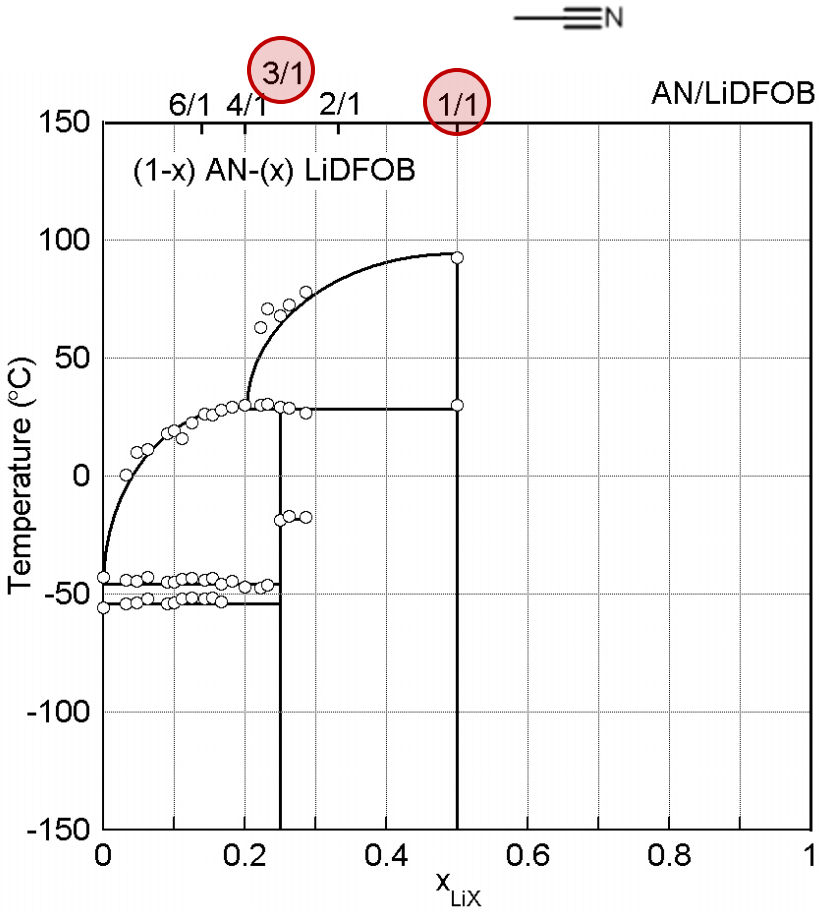
AGG-II $(AN)_1$:$LiBF_4$





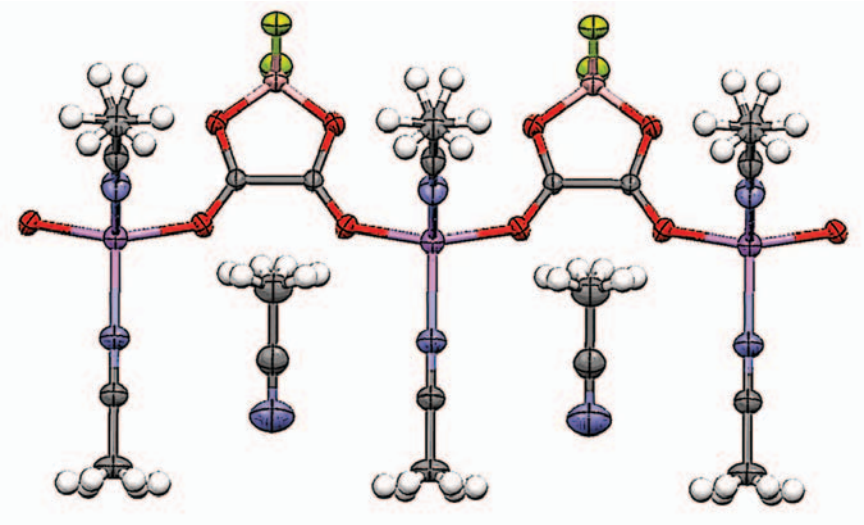
Acetonitrile $(AN)_n$-LiDFOB Phase Behavior

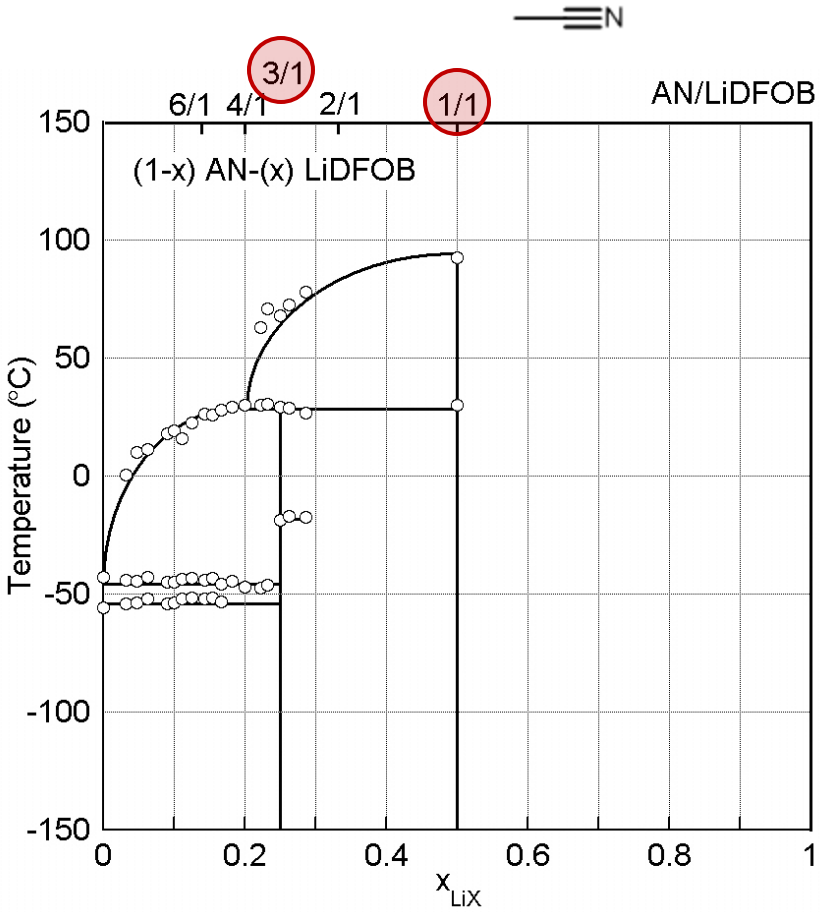




Acetonitrile $(AN)_n$-LiDFOB Phase Behavior

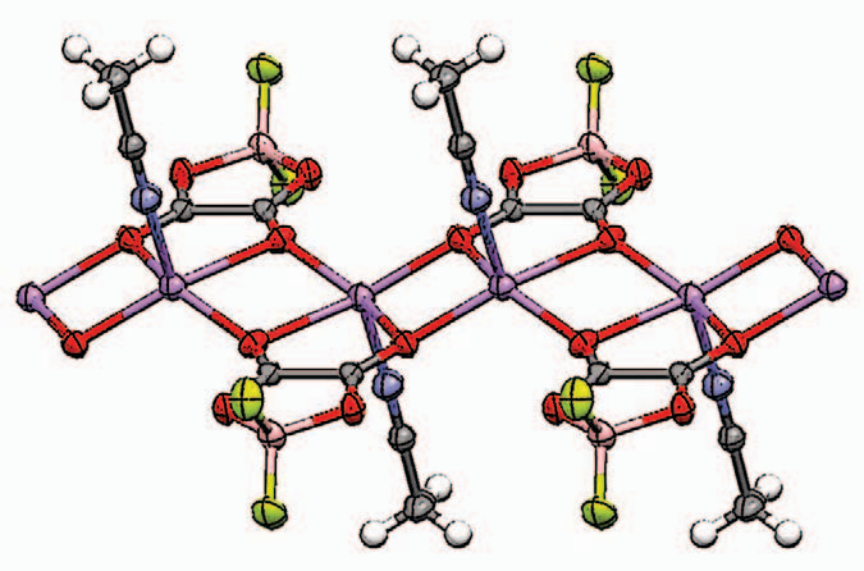
AGG $(AN)_3$:LiDFOB

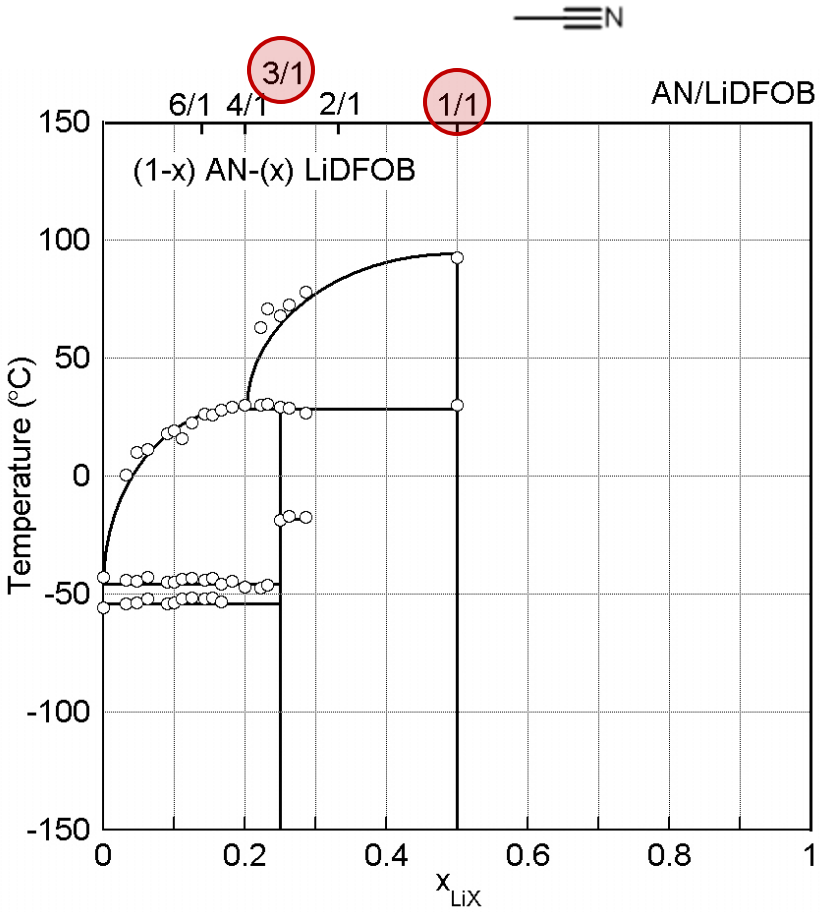




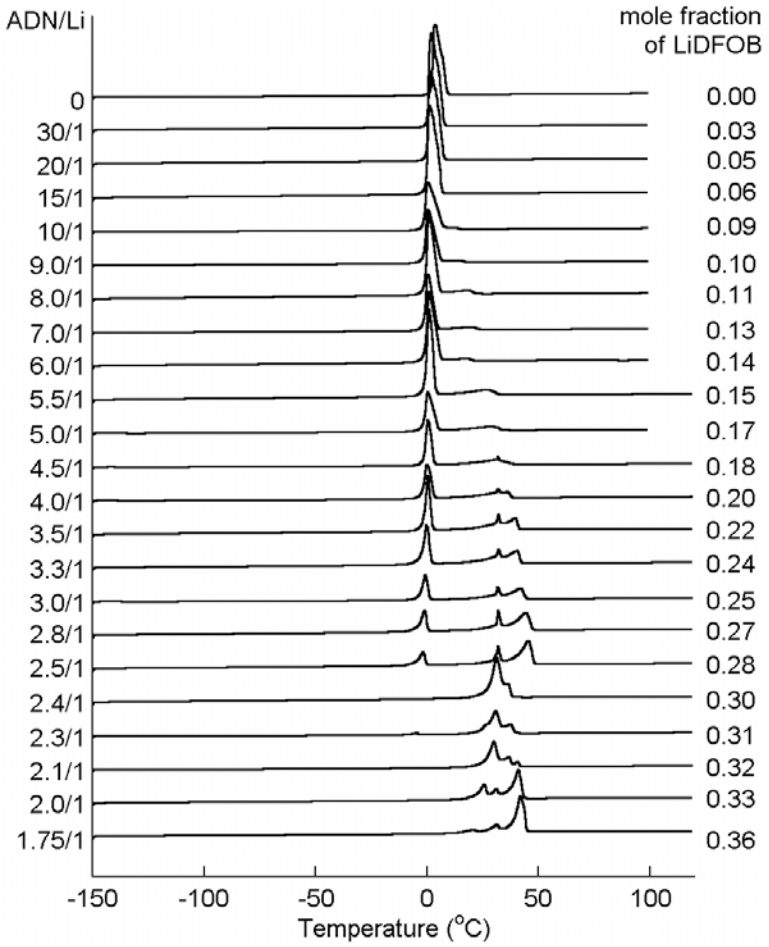
Acetonitrile $(AN)_n$-LiDFOB Phase Behavior

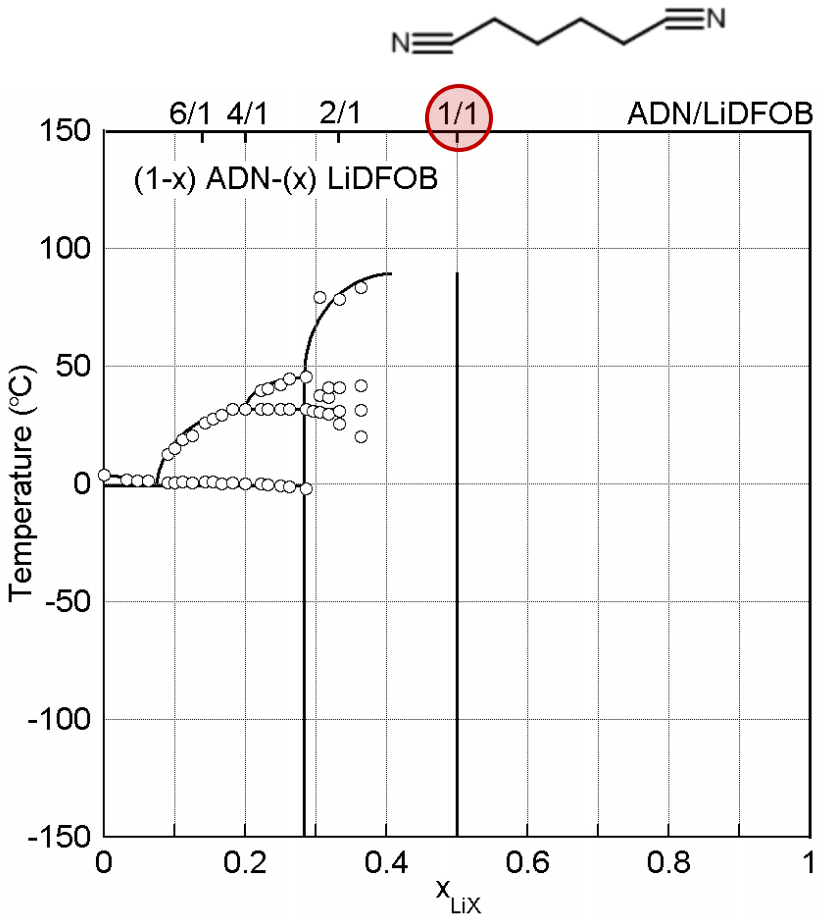
AGG $(AN)_1$:LiDFOB



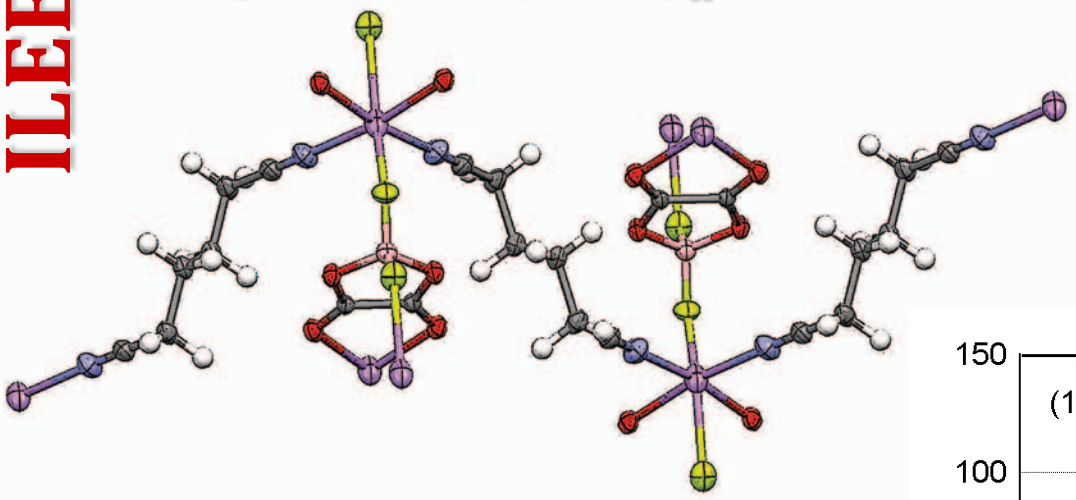


Adiponitrile $(ADN)_n$-LiDFOB Phase Behavior

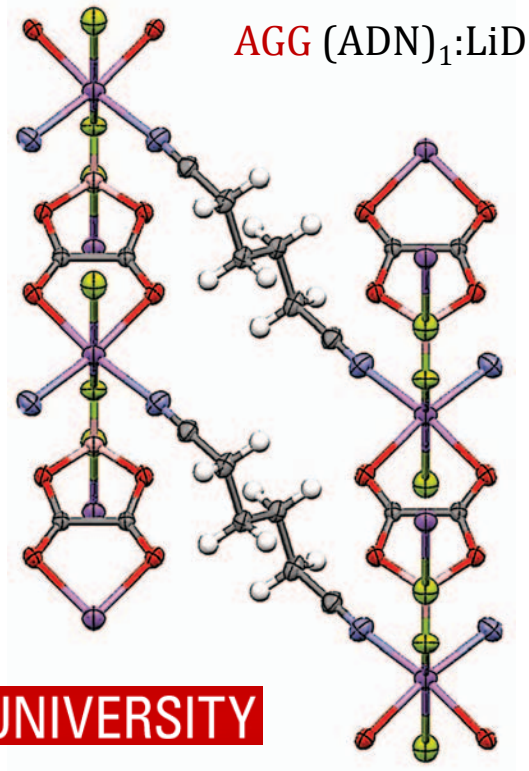


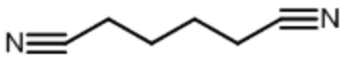


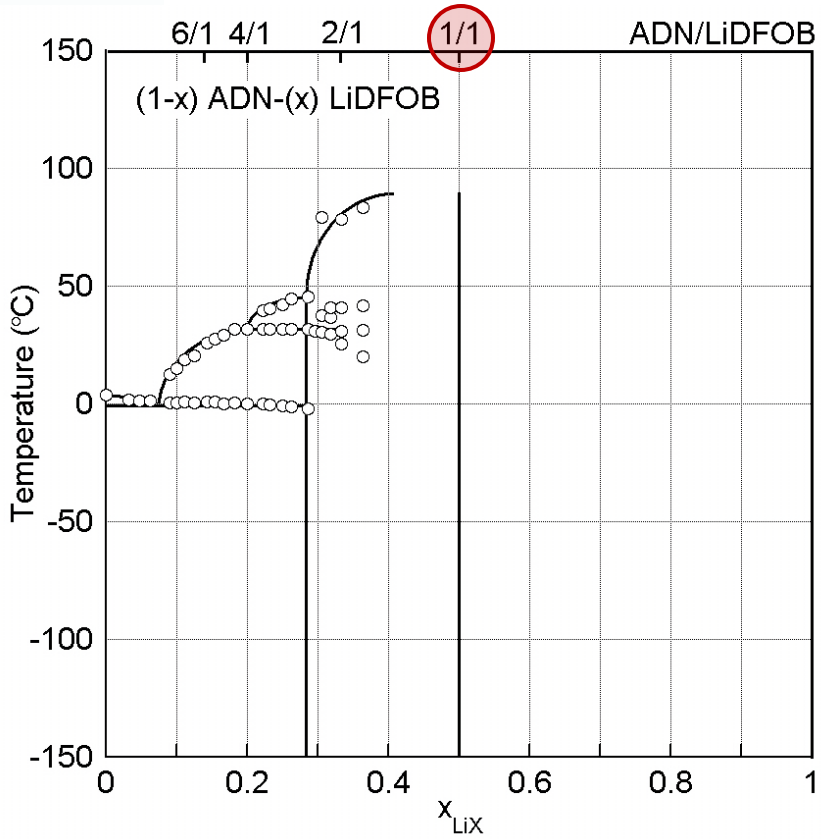
Adiponitrile $(ADN)_n$-LiDFOB Phase Behavior



AGG $(ADN)_1$:LiDFOB







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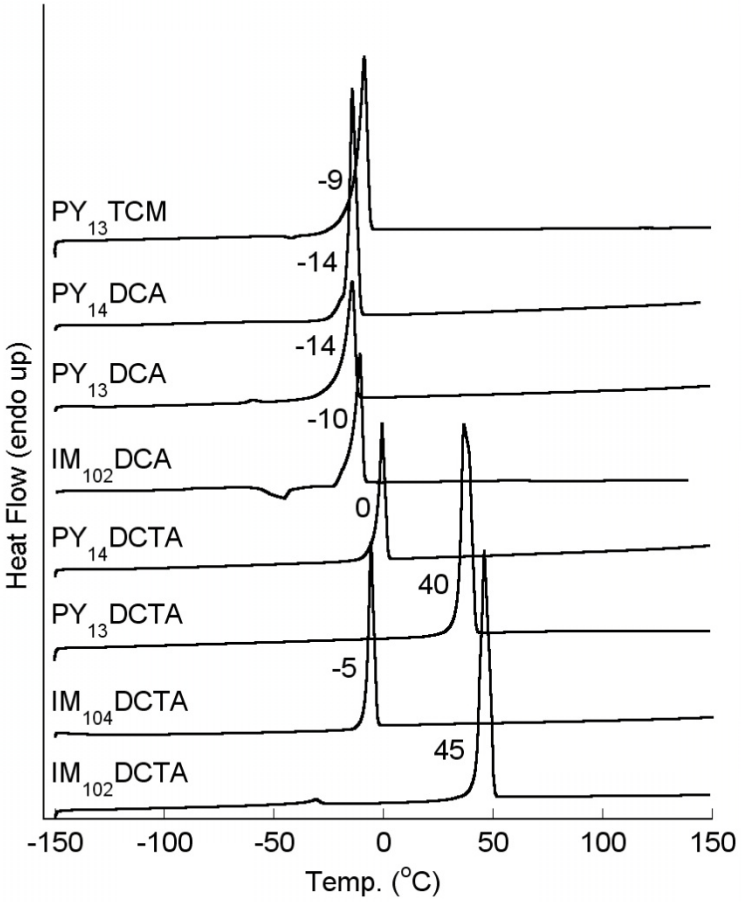
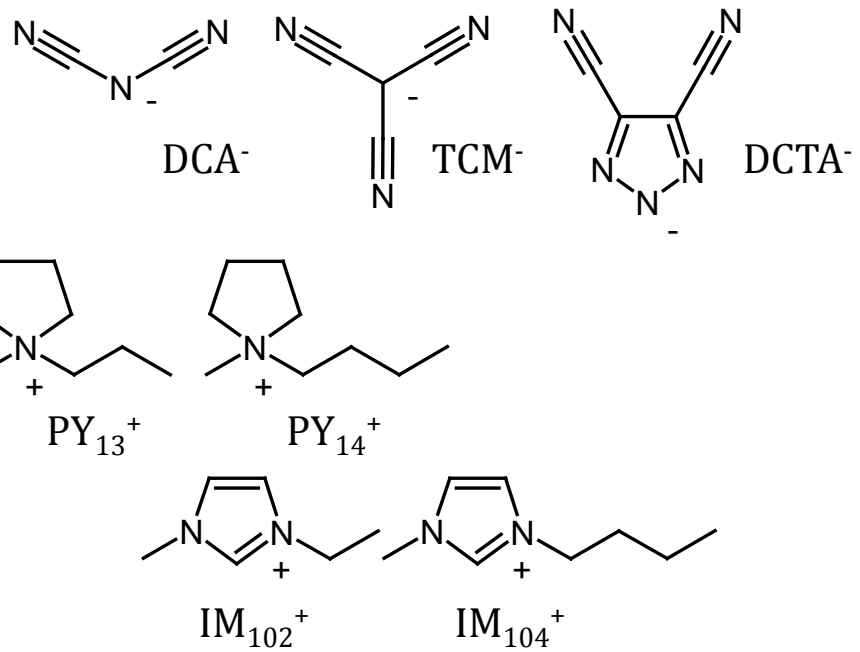
Ionic Liquids (ILs)

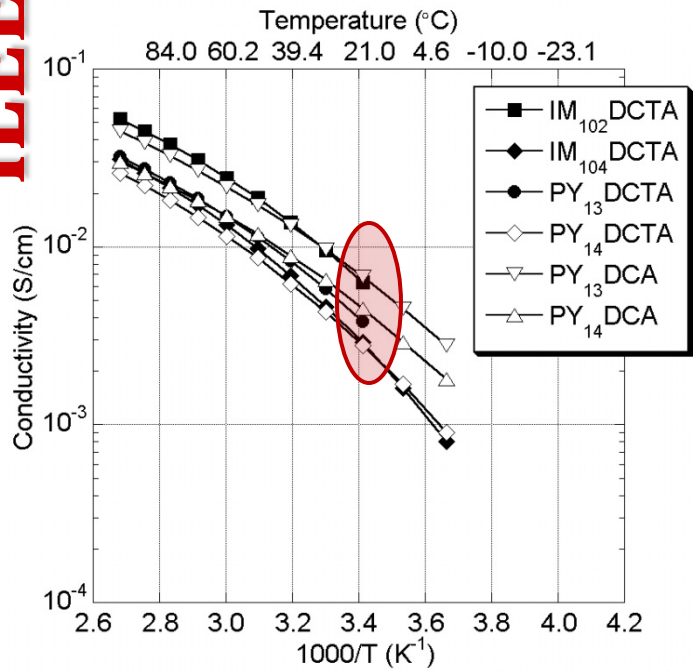
A number of ILs have been synthesized and their properties are currently being characterized

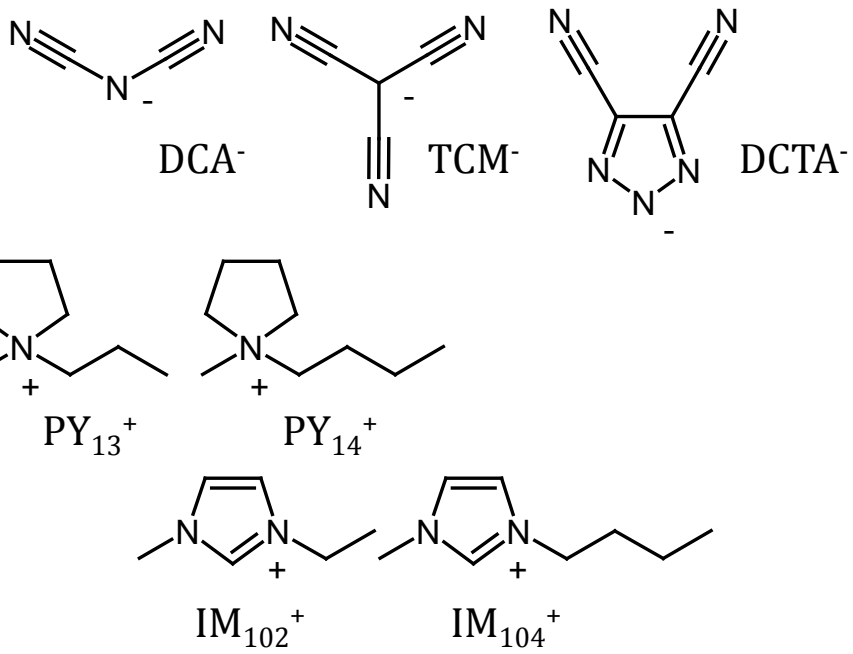


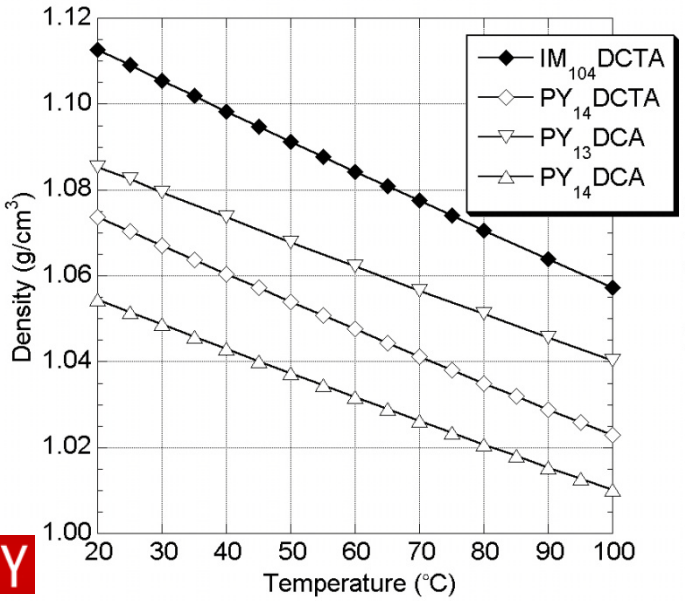


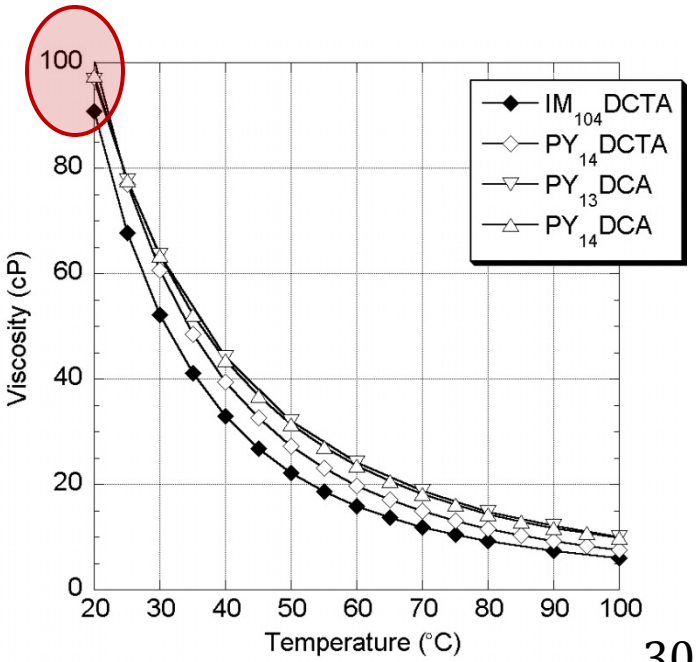
★ $IM_{10R}X$ ILs prepared for comparison with $PY_{1R}X$ ILs rather than as electrolyte materials

Ionic Liquids (ILs)









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Collaborations/Coordination with Other Institutions

Army Research Laboratory (ARL) – Joshua Allen (a graduate student) spent several weeks last year with Kang Xu and Richard Jow and will spend several months this year at ARL testing the properties of the salts

Université Paris-Sud & Hunter College of CUNY – Patrick Judeinstein and Steve Greebaum have performed NMR diffusion measurement on the ILs

Chalmers University, Sweden – Patrik Johansson is utilizing the known LiDFOB solvate structures to computationally analyze the Raman and IR vibrational bands for the different $DFOB^-$ solvate structures

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Future Work

- Continue with the phase diagram characterization of $LiBF_4$ and LiDFOB with a wide variety of solvents – extend this to include $LiPF_6$ and additional organoborate anions
- Utilize Raman spectroscopy to further characterize the solvent and anion interactions in both the solid and liquid state...correlate this work with the phase diagrams and solvate crystal structures
- Measure the transport properties (viscosity, conductivity, diffusion coefficients) of the solvent-LiX mixtures to determine the link between properties and structure (solvent and anion)
- Prepare/characterize ILs based upon the $DFOB^-$ anion with varying cations – prepare phase diagrams of IL-LiX mixtures
- Test solvent-LiX (nitrile/dinitrile) and IL-LiX mixtures in half and full cells

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Summary

- Phase diagrams have been prepared for $(solvent)_n$-$LiBF_4$ and -LiDFOB mixtures to characterize the solid-liquid thermal phase behavior – these diagrams, in concert with solvate crystal structures, provide tremendous insight into the solvent...Li^+ and anion...Li^+ interactions
- The phase diagrams and solvate structures also greatly aid in interpreting Raman vibrational spectroscopic data used to characterize the solvent and anion interactions in both the solid and liquid phase – this enables the direct exploration of detailed solution structural information – a daunting challenge to date
- Characterization of the thermal and transport properties (T_m, density, viscosity, conductivity, diffusion coefficients) of ILs is underway

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- Joshua Allen (graduate student)
- Sang-Don Han (graduate student)

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